International Journal of Medicine and Pharmaceutical Sciences (IJMPS)
ISSN(P): 2250-0049; ISSN(E): 2321-0095
Vol. 5, Issue 4, Aug 2015, 1-10

STEREOCHEMICAL AND THERAPEUTICAL STUDIES ON MN (II), CO (II) AND NI (II) COMPLEXES WITH PYRAZINE-2-CARBOXYLIC ACID HYDRAZIDE AND ITS DRAZONES

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ABSTRACT

Pyrimidine and its derivatives are of considerable biological significance. Many pyrimidine derivatives exhibit antithrombotic activity[1]. They are also used as antimicrobial, antibacterial and antimalarial drugs. Some pyrimidyl ureas and thioureas are also used as effective herbicides[2-4]. Metal complexes with 1,1-(2,6-pyrimidyl) bis benzothiazole-2-thione with transition metal ions have been isolated and characterised by different physico chemical methods[5]. **pyrazinoyl hydrazone) ($C_{13}H_{12}N_4O_3$); (N,N-Diethyl amino benzylidene-2-pyrazinoyl hyd razone) ($C_{16}H_{19}N_5O$); (cinnamalidene2-pyrazi** noyl hydrazone) ($C_{14}H_{12}N_4O$); 4-methyl salicylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_2$) and 2-Furfuralidene-2'-pyrazinoyl hydrazohe ($C_{11}H_{10}N_4O_2$) are calculated at room temperature and are[6,7] found in the range . The room temperature magnetic moment (4.40-4.88 B. M.) of the Co(II) complexes(8) is slightly lower than the normal value for an octahedral Co(II) complexes. The magnetic moment of Ni(II) complexes (2.14-3.04 B. M.) is consistent with the proposed octahedral structure[9,0].

KEYWORDS: Pyrazinoyl Hydrazone. N, N-Diethyl Amino Benzylidene-2-Pyrazinoyl Hyd Rezone

INTRODUCTION

Pyrimidine and its derivatives are of considerable biological significance. Many pyrimidine derivatives exhibit antithrombotic activity[1]. They are also used as antimicrobial, antibacterial and antimalarial drugs. Some pyrimidyl ureas and thioureas are also used as effective herbicides[2-4]. Metal complexes with 1,1-(2,6-pyrimidyl) bis benzothiazole-2-thione with transition metal ions have been isolated and characterised by different physico chemical methods[5].

The results reveal that the ligand is coordinating through pyrimidine-N- and thiocarbonyl S-atoms of the mercapto benzothiazoly group. Considerable interest has been shown in the study of the complexes of transition metal ions with various aromatic and heterocyclic derivatives of pyrazine-2-carboxylic acid hydrazide It is mainly due to potentially multidentate ligational behaviour of these pyrazine-2-carboxylic acid hydrazides. More recently interest has been growing in the synthesis and studies on physiological effects of tuberculostatic metal complexes. In many cases an increase in the tuberculostatic activity is observed when the organic derivative is complexed with a transition metal ion.

In this chapter Mn(II), Co(II) and Ni(II) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives with benzaldehyde, anislclehyde, vanilline, p-(N,N-diethylamino) benzaldehyde, cinnamaldehyde 4-methyl salicylaldehyde and furturaldehyde have been prepared. Isolated complexes have been characterised on the basis of different physico-chemical methods.

MATERIALS AND METHODS

Synthesis of Manganese (II) Complexes with Pvrazine-2-Carboxylic Acid Hydrazide and its Hydrazones

An ethanolic solution of an appropriate ligand (pyrazine-2- carboxylic acid hydrazide and its derivatives) was added with shaking to a solution of manganese chloride, in a 1:2 molar ratio at pH 10.0. The resulting solution was refluxed at 80°C for one hour, where by a colored solid gets precipitated. The precipitates were filtered by suction, washed 4-5 times with aqueous ethanol and finally with ether and dried in vacuo at room temperature to a constant weight. The analytical data for the resulting compounds are given in tabular form.

Synthesis of Cobalt(II) Complexes with Pyrazine-2-Carboxylic Acid Hydrazide and its Hydrazones

An ethanolic solution of an appropriate ligand (pyrazine-2-carboxylic acid hydrazide and its derivative) was added with shaking to a solution of managese chloride, in a 1:2 molar ratio at pH 10.0 The resulting solution was refluxed at 80^0C for one hour, where by a coloured solid gets precipitated. The precipitates were filtered by suction, washed 4-5 times with aqueous ethanol and finally with ether and dried in vacuo at room temperature to a constant weight. The analytical data for the resulting compounds are given in tabular form

Synthesis of Nickel (II) Complexes with Pyrazine-2-Carboxylic Acid Hydrazide and its Hydrazones

The ligand solution hydrazide and hydrazone (2.5 m mol) in ethanol (150 ml) was mixed with a solution of nickel chloride hydrate in 1:2 (metal:ligand) molar ratio in the same solvent. The solution was refluxed with stirring for two hour. The coloured product which appeared was filtered and washed with acetone and finally dried in vacuo. The elemental analysis and physical measurements were performed as usual. All the complexes are stable at room temperature and decompose at high temperature. Complexes are insoluble in water and common organic solvent such as benzene, xylene, toluene, ethanol, chloroform and methanol, but are soluble in DMF, DMSO 'and acetonitrile without any change in colour. Their molar conductance values in 10^{-3} M DMF are indicative of r non ionic nature

RESULTS AND DISCUSSIONS

The analytical and physical data of the compounds under study are given in table. The analytical results are in good agreement with the proposed compositions of the ligand and the metal complexes. The complexes are isolated in good yield. The complexes are fairly stable in solid phase as well as in solution phase. They are characterised by elemental analysis, infrared and electronic spectral data, conductance measurements were performed at room temperature in DMSO using a Toshniwal conductivity bridge and a dip type cell with a smooth platinum electrode. The molar conductance of these complexes lies in the range 1.80 - 11.72 ohm^{-1} cm^2 $mole^{-1}$ and suggests them to be now electrolytes. However $[Mn(C_{11}H_{10}N_4O_2)_2]Cl_2$, $[Co(C_{11}H_{10}N_4O_2)_2]Cl_2$, and $[Ni(C_{11}H_{10}N_4O_2)_2]Cl_2$, behaves as 1:2 electrolytes.

Magnetic Susceptibility Studies

The observed magnetic moments of the Mn(II) complexes with pyrazine-2-carboxylic acid hydrazide and its derivatives namely benzylidene-2-pyrazinoyl hyd razone ($C_{12}H_{10}N_4O$); (p-methoxy benzyline-2- pyrazinoyl hyd razone) ($C_{13}H_{12}N_4O_2$); (4-hydroxy-3-methoxy- benzylidene-2- pyrazinoyl hydrazone) ($C_{13}H_{12}N_4O_3$); (N,N-Diethyl amino benzylidene-2-pyrazinoyl hyd razone) ($C_{16}H_{19}N_5O$); (cinnamalidene2-pyrazi noyl hydrazone) ($C_{14}H_{12}N_4O$); 4-methyl salicylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_2$) and 2-Furfuralidene-2'-pyrazinoyl hydrazohe ($C_{11}H_{10}N_4O_2$) are calculated at room temperature and are[6,7] found in the range (5.40-6.06 B. M.). The room temperature magnetic moment

(4.40-4.88 B. M.) of the Co(II) complexes(8) is slightly lower than the normal value for an octahedral Co(II) complexes. The magnetic moment of Ni(II) complexes (2.14-3.04 B. M.) is consistent with the proposed octahedral structure[9,0].

ELECTRONIC SNECTRAL STUDIES

Manganese(II) Complexes

In the weak octahedral field, the Mn(II) complexes have ground state $(t_{2g})^3$ $(e_g)^2$ with five unpaired electrons, having 5.92 B. M., where as in the strong field in octahedra[11-13] complexes, the ground state assumes $(t_{2g})^5$ with only one unpaired electron. The Mn(II) complexes also shows two bands around 18500-19000 cm' and 2270023800 cm' assignable to $^6A_{1g}(G)\rightarrow{}^4T_{1g}(G)$ & $^6A_{1g}(G)\rightarrow{}^4T_{2g}(G)$ respectively[14,5].

Cobalt(II) Complexes

The electronic spectra of Co(II) complexes show two bands in the region 8000-9200 cm^{-1} and 17000-19000 cm^{-1} assignable to $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4T_{2g}(F)\rightarrow{}^4T_{1g}(P)$ transitions respectively, which are suggestive of an octahedral environment around the metal ion[21,22]. The different calculated values of ligand field parameters such as B_{35}, B_{35}, F_2 and F_4 also point towards the octahedral stereochemistry around the metal ion.

Nickel(II) Complexes

The Ni(II) complexes of pyrazine-2-carboxylic acid hydrazide ($C_5H_6N_4O$) benzylidene-2-pyrazi noyl hydrazone ($C_{12}H_{10}N_4O$); Anisalidene-2razinoyl hydrazone ($C_{13}H_{12}N_4O_2$); 4-hydroxy-3-methoxy benzylidene-2yrazinoylhydrazone($C_{13}H_{12}N_4O_3$) N-N'-Diethyl amino benzylidene- -pyrazinoyl hydrazone ($C_{16}H_{19}N_5O$); cinnamalidene-2-pyrazinoyl hydrazone $C_{14}H_{12}N_4O$) 4-methyl salicylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_2$) and rfurali-dene-2'-pyrazinoyl hydrazone ($C_{11}H_{10}N_4O_2$) have been assigned an octahedral geometry on the basis of their electronic spectrum which shows two bands around 18000 and 26000 cm^{-1} assigned to the $^3T_{1g}(F)\leftarrow{}^3A_{2g}$ and $^3T_{2g}(F)^3A_{2g}$ transitions respectively, which are characteristic of an octahedral structure. The values of various ligand field parameters 10 Dq, B_{35}, F_2, F_4 and L.F.S.E. are found in the range expected for octahedral stereochemistry [23].

INFRA RED SPECTRAI STUDIES

A study and comparison of the infrared spectra of free ligands pyrazi ne-2-carboxylic acid hyd razide ($C_5H_6N_4O$); benzylidene-2-pyrazi noylhydrazone ($C_{12}H_{10}N_4O$); Anisalidene-2-pyrazinoyl hyd razone ($C_{13}H_{12}N_4O_2$); 4-ydroxy-3-rnethoxy benzylidene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_4O_3$); N-Diethyl amino benzylidene-2-pyrazinoyl hyd razone ($C_{16}H_{19}N_5O$); cinnamalidene-2-pyrazi noyl hydrazone ($C_{14}H_{12}N_4O$); 4-methyl salicylicdene-2-pyrazinoyl hydrazone ($C_{13}H_{12}N_40_2$) and 2-furfuralidene-2'-pyrazinoyl hydrazone ($C_{11}H_{10}N_4O_2$) and their Mn(II), Co(II) and Ni(II) complexes (data summarized in table 3 8, 3.9 and 3.10) imply that the possible donor sites in all of the proposed ligands are amido (-C=O) oxygen and azomethine terminal nitrogen assigning their bidentate character while in 4-methyl-salicylidene-2-pyrazi noyl hyd razone ($C_{13}H_{12}N_4O_2$)and 2-furfura- lidene-2'-pyrazinoyl hydrazone (C11H10N4O_2), one more coordinating site was observed, so revealing their tridentate character. The absorption band observed at 3500 cm' and 3450 cm ($C_{13}H_{12}N_4O_3$) and ($C_{13}H_{12}N_4O_2$) respectively are tentatively assigned to v(OH) attached to the phenyl ring in the free ligand ($C_{13}H_{12}N_4O_2$) shows a characteristic decrease in intensity as well as in the frequency nearly 40 cm^{-1} in the IR-spectra of the complexes, showing theirby participation of phenolic group in chelation. The shifts in the band positions in the JR-spectra of the complexes of these metal ions have been found to be similar. The following are the general observations in their spectra (i). The □(NH) of the ligand at 3200 cm^{-1} do not shift or disappeared in the spectra of all the complexes suggesting

non participation of vNH.[24]

- The amide band I □(C=O) in the complexes was shifted to lower wave numbers (Δ□ = 30 cm^{-1}) indicating the involvement of carbonyl oxygen in bond formation[25].
- The position of the amide bands having contribution from □(C=N), δ(N-H) in the region 1500 to 1000 cm^{-1} either did not shifted or the shifts were too small to draw any definite conclusions from the direction of shifts.
- The ligands exhibit the □(C=N) in the region 1605-1645 cm^{-1} and the band shifts to lower energy side in complexes indicating nitrogen coordination[26].

[(Co($C_5H_6N_4O)_2Cl_2$.]

The compound was found thermally stable upto 330°C and mass loss takes place rapidly in the temperature ranje 350-650°C. The complex decomposes into oxide at 650°C. The fraction decomposed □=0.75 corresponds to the decomposition of this complex into $C0_20_3$. The DTA curve, shows the endothermal peaks at 160°C and 270°C corresponding to the melting point of the complex, the exothermal peaks at 380°C and 640°C corresponds to the complete burning of the organic portion of the complex[4

[6]**[Ni($C_{13}H_{12}N_4O_2)_2Cl_2$]**

From the TG curve it was observed that the complex is stable upto 160°C and mass loss takes place rapidly in the temperature range 300-450°C. The complex decomposes into oxide at 600°C. Ihe fraction decomposed corresponds (α=0.74) to the decomposition of the complex in Ni_2O_3. The DTA curve shows the endothermal peaks at 170°C. 420°C and 540°C corresponding to the melting of the complex, the exothermal peaks at 390 and 460°C corresponds to the burning of the wganic portion of the complex[47]

Table 1: Thin-Layer Chromatographic Screening of Mn (II), Co (II) And NI (II) Complexes Using T_1 Methanol Ammonia Solution, Strong (100:1.5) T_2 Acetic Acid Glacial : Benzene (1:9), T. Ammonia Solution Strong: Ethanol (90 Percent) : Dioxane (5:60:35), T_3 – Acetic Acid Glacial : Ethanol (90 Percent) Water (30:60:10), T_5-N- Butyl Alcohol:Methanol (40:60) and T_6- Ammonia Solution, Strong: Benzene: Dioxane : Ethanol (90 Percent) (5:50:40:5) as Mobile Phase

S.No.	Compound	R_fx100					
		Solvent System I	Solvent System II	Solvent System III	Solvent System IV	Solvent System V	Solvent System VI
1.	[Mn($C_5H_6N_4O)_2Cl_2$]	75.6	3.4	68.1	57.8	32.6	4.2
2.	[Mn($C_{12}H_{10}N_4O)_2Cl_2$]	85.5	4.4	64.2	61.3	56.2	49.6
3.	[Mn($C_{13}H_{12}N_4O_2)_2CL_2$]	84.8	3.0	67.5	60.6	64.8	42.2
4.	[Mn($C_{13}H_{12}N_4O_3)_2CL_2$]	81.7	1.2	51.6	62.1	52.5	12.4
5.	[Mn($C_{16}H_{19}N_5O)_2CL_2$]	85.1	2.0	65.3	63.3	61.0	4.0
6.	[Mn($C_{13}H_{11}N_4O_2)_2$]	80.6	1.8	66.1	65.1	56.0	9.7
7.	[Mn($C_{11}H_{10}N_4O_2)_2$]CL_2]	82.0	2.0	57.1	66.0	58.8	26.0
8.	[Co($C_{13}H_{12}N_4O_2)_2CL_2$]	82.2	2.6	87.0	60.0	60.5	45.2
9.	[Co($C_{13}H_{12}N_4O_3)_2CL_2$]	83.3	0.6	53.0	62.0	57.5	12.2
10.	[Ni($C_{13}H_{12}N_4O)_2CL_2$]	81.4	3.0	65.0	60.8	64.8	41.6
11.	[Ni($C_{16}H_{19}N_5O)_2CL_2$]	85.2	1.4	56.0	65.6	58.8	41.8

(a) Silica getl-G (incorporating 13% calcium sulphate as binder) was used as absorbent.
(b) The spots were detected by iodine vapours.

Table 2: Analytical and Magnetic Data of Manganese (II) Complexes with Pyrazine-2-Carboxylic Acid Hydrazide and its Derivatives

S. No.	Compounds Colour,M.P./ D.T.* ^{0}c	Molar Conductance In 10^{-3} M Dmf Ohm^{-1} Cm^{-2} Mol^{-1}	% Elemental Analysis (Found/Calcd.)					Effective Magetic Moment μ_{eff} (Corr.)B.M. (At 300 $\pm$ 1^0k)	Stereochemistry
			C	H	N	Cl	m		
1	2	3	4	5	6	7	8	9	10
1	$[Mn(C_5H_6N_4O)_2Cl_2]$ off white 142	8.4	29.75 (29.85)	2.90 (2.98)	27.75 (27.86)	17.58 (17.66)	13.60 (13.66)	5.78	H S O
2	$[Mn(C_{12}H_{10}N_4O)_2Cl_2]$ white 164	9.0	49.70 (49.83)	3.40 (3.46)	19.28 (19.37)	12.20 (12.28)	9.40 (9.50)	5.40	H S O
3	$[Mn(C_{13}H_{12}N_4O_2)_2CL_2]$ white 145	2.0	48.80 (48.90)	3.70 (3.76)	17.50 (17.55)	11.05 (11.12)	8.54 (8.61)	5.84	H S O
4	$[Mn(C_{13}H_{12}N_4O_3)_2CL_2]$ Yellow 142	8.6	46.48 (46.57)	3.48 (3.58)	16.60 (16.71)	10.50 (10.59)	8.04 (8.20)	5.80	H S O
5	$[Mn(C_{16}H_{19}N_5O)_2CL_2]$ Orange >300	4.5	53.25 (53.33)	5.20 (5.27)	19.37 (19.44)	9.78 (9.86)	7.52 (7.63)	5.92	H S O
6	$[Mn(C_{14}H_{12}N_4O)_2Cl_2]$ Light yellow >310	6.8	53.25 (53.33)	3.70 (3.80)	17.66 (17.77)	11.20 (11.27)	8.65 (8.72)	5.83	H S O
7	$[Mn(C_{13}H_{11}N_4O_2)_2]$ Light yellow 170	8.2	55.15 (55.22)	3.80 (3.89)	19.75 (19.82)	---	9.65 (9.72)	6.06	H S O
8	$[Co(C_{11}H_{10}N_4O_2)_2CL_2]$ Brown 172	90.20	44.93 (45.05)	3.35 (3.41)	19.07 (19.11)	12.05 (12.11)	9.28 (9.37)	5.75	H S O

H S O- HIGH Spin Octahedral

Table 3: Analytical and Magnetic Data of Cobalt (II) Complexes With Pyrazine-2- Carboxylic Acid Hydrazide and its Derivatives

S. No.	Compounds Colour,M.P./ D.T.* ^{0}c	Molar Conductance In 10^{-3} M Dmf Ohm^{-1} Cm^{-2} Mol^{-1}	% Elemental Analysis (Found/Calcd.)					Effective Magetic Moment μ_{eff} (Corr.)B.M. (At 300 $\pm$ 1^0k)	Stereo-Chemistry
			C	H	N	Cl	M		
1	2	3	4	5	6	7	8	9	10
1	$[Co(C_5H_6N_4O)_2Cl_2]$ Light violet 200	1.8	29.47 (29.56)	2.90 (2.95)	27.50 (27.59)	17.40 (17.49)	14.42 (14.51)	4.62	H S O
2	$[Co (C_{12}H_{10}N_4O)_2Cl_2]$ Blue >290	4.2	49.40 (49.49)	3.34 (3.43)	19.18 (19.24)	12.05 (12.20)	10.04 (10.12)	4.60	H S O
3	$[Co (C_{13}H_{12}N_4O_2)_2CL_2]$ Green 285	5.0	48.50 (48.60)	3.65 (3.73)	17.38 (17.44)	10.93 (11.06)	9.02 (9.18)	4.40	H S O
4	$[Co (C_{13}H_{12}N_4O_3)_2CL_2]$ Light green 250*	6.6	46.20 (46.29)	3.46 (3.56)	16.52 (16.61)	10.44 (10.53)	8.65 (8.74)	4.48	H S O
5	$[Co (C_{16}H_{19}N_5O)_2CL_2]$ Brown 262	7.5	52.94 (53.04)	5.15 (5.24)	19.22 (19.33)	9.70 (9.80)	8.06 (8.14)	4.76	H S O
6	$[Co (C_{14}H_{12}N_4O)_2Cl_2]$ Light brown 280*	8.20	52.90 (53.00)	3.70 (3.78)	17.58 (17.66)	11.10 (11.19)	9.20 (9.29)	4.70	H S O
7	$[Co (C_{13}H_{11}N_4O_2)_2]$ Brown 270	9.2	54.73 (54.83)	3.75 (3.86)	19.60 (19.68)	---	10.28 (10.35)	4.88	H S O
8	$[Co(C_{11}H_{10}N_4O_2)_2CL_2]$ Light brown 250	168.84	44.65 (45.75)	3.30 (3.39)	19.90 (19.98)	11.95 (12.03)	9.89 (9.98)	4.76	H S O

H S O- HIGH Spin Octahe

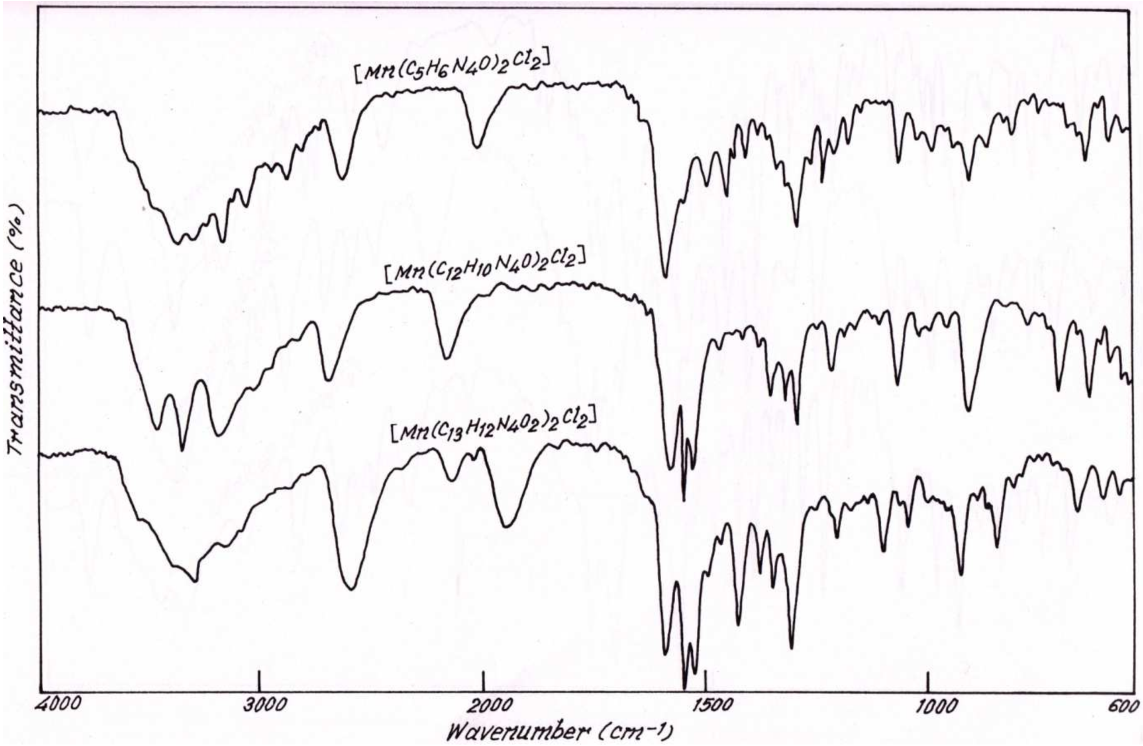

Figure 1: I. R. Spectra of Mn(11) Complexes

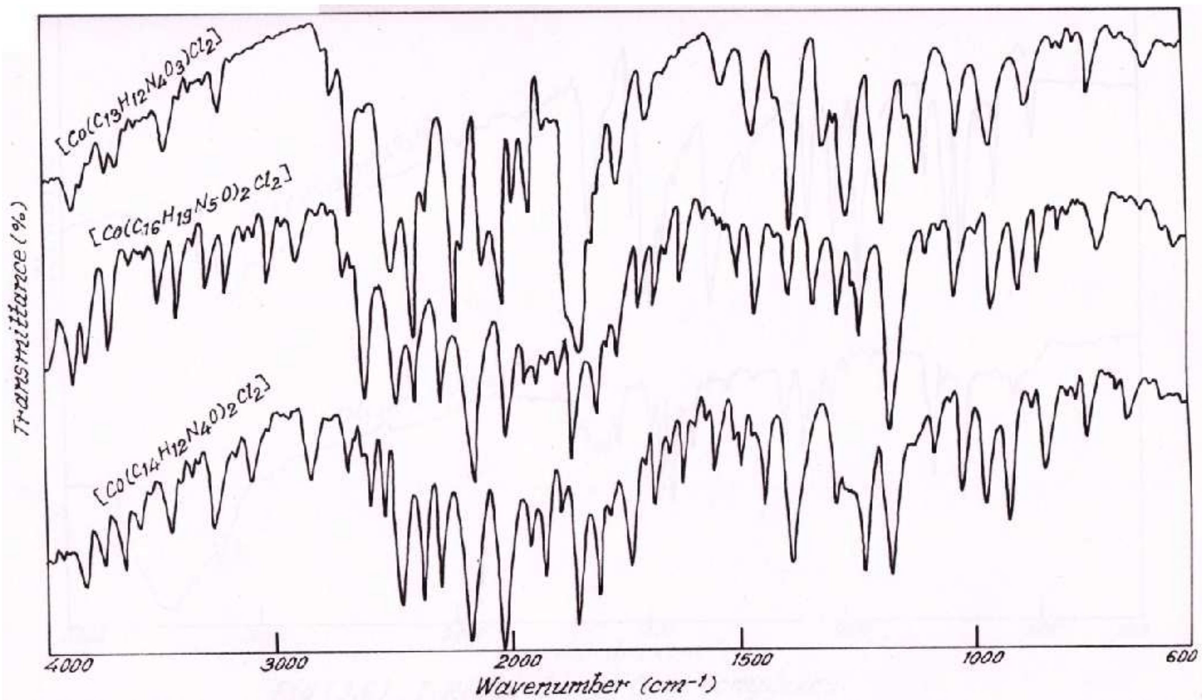

Figure 2: I. R. Spectra of Co(11) Complexes

Table 4: Selected I.R Frequencies (Cm-1) and their Tentative Assignment from I. R. Spectra of Nickel (II) Complexes with Pyrazoline-2- Carboxylic Acid Hydrazide and its Derivative

S. No.	Compound	Amide Band I □(C=O)	Amide Band Ii □(-Ch=N-) Of Immine- Nh Bending Modes	Antisymmetric & Symmetric □ (C=C)+□ □(C=N)Of Pyrazine Ring	Amide Band Iii □(C+O) + □(C+O)+ γ(O) + γ (Cn)	Amide Band Iv γ (Nco)+ γ (C-O)	Pyrazine Ring Breathings, Deformation Δ(N-N)*	Metal Donor Frequencies 1.□(M-Azomethine- N) 2.□(M-Enolic-O) 3.□(M-Halogen)
1	2	3	4	5	6	7	8	9
1	$[Ni(C_5H_6N_4O)_2Cl_2]$	1640vs 1600vs	1580ms	1565sh 1540ms	1370ms	1130vs	1030vs 885vs*	1. 480ms 2. 330m 3. 280m
2	$[Ni\,(C_{12}H_{10}N_4O)_2Cl_2]$	1610vs	1590vs 1575ms	1550ms	1400ms 1360vs	1200vs 1175ms 1150vs	1065ms 1030s 885s*	1. 470m 2. 340m, 3. 285s
3	$[Ni\,(C_{13}H_{12}N_4O_2)_2CL_2]$	1610vs	1580vs	1555ms 1515s	1400ms 1360sh 1335ms	1205vs 1180ms 1130s	1070ms 890vs*	1. 475m 2. 330m 3. 280s
4	$[Ni\,(C_{13}H_{12}N_4O_3)_2CL_2]$	1600ms 1600sh	1575ms	1560sh 1510vs	1420vs 1335ms	1215ms 1180vs 1145ms	1060vs 1015ms 900vs*	1. 470m 2. 340m 3. 270s
5	$[Ni\,(C_{16}H_{19}N_5O)_2CL_2]$	1620vs 1600sh	1570vs	1520s	1390ms	1210ms 1165s 11140s	1050ms 1025s 9055s*	1. 475ms 2. 340ms,330s 3. 280 ms

s-sharp ms-medium sharpvs-very sharp sh-shoulder b-broad vb-very broad

Table 5: Selected I.R Frequencies (Cm-1) and their Tentative Assignment from I.R. Spectra of Nickel(II) Complexes with Pyrazoline-2- Carboxylic Acid Hydrazide and its Derivative

S. No.	Compound	Amide Band I □(C=O)	Amide Band Ii □(-Ch=N-) Of Immine- Nh Bending Modes	Antisymmetric & Symmetric □ (C=C)+□ □(C=N)Of Pyrazine Ring	Amide Band Iii □(C+O) + □(C+O)+ γ(O) + γ (Cn)	Amide Band Iv γ (Nco)+ γ (C-O)	Pyrazine Ring Breathings, Deformation Δ(N-N)*	Metal Donor Frequencies 1.□(M-Azomethine- N) 2.□(M-Enolic-O) 3.□(M-Halogen)
1	2	3	4	5	6	7	8	9
1	$[Ni(C_5H_6N_4O)_2Cl_2]$	1640vs 1600vs	1580ms	1565sh 1540ms	1370ms	1130vs	1030vs 885vs*	1. 480ms 2. 330m 3. 280m
2	$[Ni\,(C_{12}H_{10}N_4O)_2Cl_2]$	1610vs	1590vs 1575ms	1550ms	1400ms 1360vs	1200vs 1175ms 1150vs	1065ms 1030s 885s*	1. 470m 2. 340m, 3. 285s
3	$[Ni\,(C_{13}H_{12}N_4O_2)_2CL_2]$	1610vs	1580vs	1555ms 1515s	1400ms 1360sh 1335ms	1205vs 1180ms 1130s	1070ms 890vs*	1. 475m 2. 330m 3. 280s
4	$[Ni\,(C_{13}H_{12}N_4O_3)_2CL_2]$	1600ms 1600sh	1575ms	1560sh 1510vs	1420vs 1335ms	1215ms 1180vs 1145ms	1060vs 1015ms 900vs*	1. 470m 2. 340m 3. 270s
5	$[Ni\,(C_{16}H_{19}N_5O)_2CL_2]$	1620vs 1600sh	1570vs	1520s	1390ms	1210ms 1165s 11140s	1050ms 1025s 9055s*	1. 475ms 2. 340ms,330s 3. 280 ms

s-sharp ms-medium sharpvs-very sharp sh-shoulder b-broad vb-very broad

Table 6: Selected I.R Frequencies (Cm-1) and their Tentative Assignment from I.R. Spectra of Nickel(II) Complexes with Pyrazoline-2- Carboxylic Acid Hydrazide and its Derivative

S. No.	Compound	Amide Band I □(C=O)	Amide Band Ii □(-Ch=N-) Of Immine- Nh Bending Modes	Antisymmetric & Symmetric □(C=C)+□ □(C=N)Of Pyrazine Ring	Amide Band Iii □(C+O) + □(C+O)+ γ(O) + γ (Cn)	Amide Band Iv γ (Nco) + γ (C-O)	Pyrazine Ring Breathings, Deformation Δ(N-N)*	Metal Donor Frequencies 1.□(M-Azomethine-N) 2.□(M-Enolic-O) 3.□(M-Halogen)
1	2	3	4	5	6	7	8	9
6	$[Ni(C_{14}H_{12}N_4O)_2Cl_2]$	1620vs 1590sh	1610sh 1580ms	1560ms	1400vs 1340ms	1200ms 1165s	1065vs 1025vs 900vs*	1. 475ms 2. 335ms,325s 3. 280m
7	$[Ni\,(C_{13}H_{11}N_4O)_2Cl_2]$	1600ms	1610ms 1585b	1530ms	1400vs 1340vs	1150s 1125b	1070s 1020vs 880vs*	1. 480m 2. 330m, 3. 275m
8	$[Ni\,(C_{11}H_{10}N_4O_2)_2CL_2]$	1630s 1600s	1590s	1550vb	1390s 1335s	1215s 1170vs 1130s	1080sh 1060vs 1020ms 900ms*	1. 470m 2. 320m 3. 230s

s-sharp ms-medium sharpvs-very sharp sh-shoulder b-broad vb-very broad

Table 7: Antitubercular Activity of Manganese (II), Cobalt (II) and Nickel (II) Complexes with Pyrazine-2-Carboxylic Acid Hydrazide and its Hydrazones Against Mycobacterium Tuberculosis

S.No.	Compounds	Concentration (Mcg/Ml)						
		100	50	25	12.5	6.25	3.0	1.5
1.	[Mn $(C_{14}H_{12}N_4O)_2CL_2$]	+	+	+	+	+	+	+
2.	[Mn $(C_{11}H_{10}N_4O)_2CL_2$]	+	+	+	+	+	+	+
3.	[Co $(C_{13}H_{12}N_4O_3)_2CL_2$]	+	+	+	+	+	+	+
4.	[Co $(C_{13}H_{11}N_4O_2)CL_2$]	+	+	+	+	+	+	+
5.	[Ni $(C_{16}H_{19}N_5O)_2CL_2$]	+	+	+	+	+	+	+

(-) Sign indicates no growth (antitubercular activity) and
(+) Sign indicates bacterial growth.

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